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**Syndiotactic styrene polymer compsn - prepared by mixing with rubber-like materials
giving enhanced impact and heat resistance.**

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Abstract

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A styrene based resin compsn. comprises (A) a styrene base resin with a mainly syndiotactic configuration at pref. 65-99 weight%; (B) a rubber like polymer at pref. 35-1 weight%; and opt. (C) an inorganic filler.

The rubber-like polymer (B) can take forms loosely categorised as (1) polymers produced from vinyl monomer polymerisation in the presence of another monomer selected from gp. consisting of alkyl acrylate, alkyl methacrylate and polyfunctional monomers having conjugated diene type double bonds. (11) polymers which are at least one graft block copolymer of a-b type, a-b-a type or a-b-a-b type, an a grafted b copolymer or a b grafted a copolymer where a is atactic polystyrene. (111) a natural or synthetic rubber.

USE/ADVANTAGE - The compsn. has enhanced impact resistance, heat resistance, tensile strength and modulus of elasticity. It is suitable for injection moulding, extrusion moulding, etc. Dwg.0/0

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(54) Styrene-based resin composition.

(57) A styrene-based resin composition containing (A) a styrene-based resin having mainly syndiotactic configuration and (B) a rubber-like polymer, or further (C) an inorganic filler. The rubber-like polymer (B) includes, for example, (I) polymers produced by polymerizing vinyl monomers in the presence of polymers obtained through polymerization of one or more monomers selected from the group consisting of alkyl acrylate, alkyl methacrylate and polyfunctional monomers having conjugated diene-type double bonds, (II) block or graft copolymers selected from an a-b type block copolymer, an a-b-a type block copolymer, a b-a-b type block copolymer, an a grafted b copolymer and a b grafted a copolymer and (III) natural or synthetic rubber. The present composition is excellent in heat resistance and further in other physical properties such as impact resistance, stiffness and so on.

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STYRENE-BASED RESIN COMPOSITION

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to a styrene-based resin composition and more particularly to a styrene-based resin composition containing a styrene-based resin having mainly syndiotactic configuration and a rubber-like polymer, which is excellent in heat resistance and impact resistance.

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2. Description of the Related Art

Styrene-based resins have a disadvantage in that impact resistance is poor. In order to improve impact resistance, copolymerization of styrene-based resins and rubber-like polymers (e.g., HIPS resin and ABS resin), or compounding rubber-like polymers to the styrene-based resins has been widely carried out.

Styrene-based resins, with improved impact resistance by compounding rubber-like polymer thereto or the above-described copolymerization, have been widely used in various applications. However, a styrene-based resin with more improved impact resistance and heat resistance is desired depending on the purpose of use thereof.

Styrene-based resins which have heretofore been used are produced by radical polymerization, have atactic configuration and furthermore are non-crystalline. Therefore, their heat resistance is not very high.

The present inventors have made extensive investigations to develop a styrene-based resin composition having physical properties markedly improved beyond the limits of properties of styrene-based resins produced conventionally. As a result, the present inventors have discovered that if a styrene-based resin of high syndiotacticity as developed by the present inventors' group (Japanese Patent Application Laid-Open No. 104818/1987) is mixed with a rubber-like polymer, there can be obtained a resin composition having these desired physical properties.

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SUMMARY OF THE INVENTION

An object of the present invention is to provide a styrene-based resin composition having excellent impact resistance.

Another object of the present invention is to provide a styrene-based resin composition having both excellent impact resistance and heat resistance.

Still another object of the present invention is to provide a styrene-based resin composition which has excellent physical properties such as tensile strength and modulus of elasticity as well as impact resistance and heat resistance.

Still another object of the present invention is to provide a styrene-based resin composition having excellent physical properties, which is suitable as a material for injection molding, extrusion molding and so forth.

The present invention relates to a styrene-based resin composition containing (A) a styrene-based resin having mainly syndiotactic configuration and (B) a rubber-like polymer as the main components.

The present invention also relates to a styrene-based resin composition containing the above Components (A) and (B), and (C) an inorganic filler as the main components.

DESCRIPTION OF PREFERRED EMBODIMENTS

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The resin composition of the present invention contains Components (A) and (B) as main components.

Component (A) is a styrene-based resin with mainly syndiotactic configuration. The styrene-based resin with mainly syndiotactic configuration refers to a polymer with mainly *st*reo structure such that phenyl groups or substituted phenyl groups as side chains are located alternately at opposite positions relative to the main chain composed of carbon-carbon bonds. The tacticity is quantitatively determined by a nuclear

- magnetic resonance method using a carbon isotope (^{13}C -NMR method). The tacticity as determined by the ^{13}C -NMR method is indicated in terms of proportions of structural units continuously connected to each other, i.e., a diad in which two structural units are connected to each other, a triad in which three structural units are connected to each other, and a pentad in which five structural units are connected to each other.
- 5 The styrene-based resin with mainly syndiotactic configuration has syndiotactic configuration such that the proportion in a diad is at least 75% and preferably at least 85%, or the proportion in a pentad (racemi pentad) is at least 30% and preferably at least 50%. The styrene-based resin includes polystyrene, poly-(alkylstyrene), poly(halogenated styrene), poly(alkoxystyrene), poly(vinyl benzoate), and their mixtures, and copolymers containing the above polymers as main components.
- 10 The poly(alkylstyrene) includes polymethylstyrene, polyethylstyrene, polyisopropylstyrene, and poly-(tert-butylstyrene). The poly(halogenated styrene) includes polychlorostyrene, polybromostyrene, and poly-fluorostyrene. The poly(alkoxystyrene) includes polymethoxystyrene and polyethoxystyrene. Of these poly-mers, polystyrene, poly(p-methylstyrene), poly(m-methylstyrene), poly(p-tert-butylstyrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), and a copolymer of styrene and p-methyl-
- 15 styrene are most preferable.
- The styrene-based resin to be used in the present invention is not critical in molecular weight. The weight average molecular weight is preferably at least 10,000 and particularly preferably at least 50,000. The molecular weight distribution is not critical and may be narrow or wide.
- The styrene-based resin to be used in the present invention can be produced, for example, by
- 20 polymerizing a styrene-based monomer (corresponding to the above styrene-based resin) with the use of a catalyst containing a titanium compound, and a condensate of water and trialkylaluminum in the presence of an inert hydrocarbon solvent or in the absence of a solvent (Japanese Patent Application Laid-Open No. 187708/1987).
- Various rubber-like polymers can be used as Component (B). The rubber-like polymers belonging to the
- 25 following Groups(I),(II) or -(III) are preferred.

Group (I)

- 30 Polymer in Group (I) are rubber-like polymers which are produced by polymerizing vinyl monomers in the presence of polymers obtained through polymerization of one or more monomer selected from the group consisting of alkyl acrylate, alkyl methacrylate and polyfunctional monomers containing a conjugated diene double bond. In the alkyl acrylate and the alkyl methacrylate, an alkyl group having 2 to 10 carbon atoms is suitable. Specific examples of the alkyl acrylate and the alkyl methacrylate are ethyl acrylate, butyl
- 35 acrylate, 2-ethylhexyl acrylate and n-octyl methacrylate.
- Examples of the polyfunctional monomers containing a conjugated diene type double bond are; conjugated diene compounds such as butadiene and isoprene, and compounds containing non-conjugated double bonds, as well as conjugated diene type double bonds, in the molecule thereof. Specific examples are 1-methyl-2-vinyl-4,6-heptadiene-1-ol, 7-methyl-3-methylene-1,6-octadiene, and 1,3,7-octatriene.
- 40 As Component (B), rubber-like polymers which are produced by polymerizing a vinyl monomer in the presence of polymers or copolymers obtained by polymerizing one of the above monomers or by copolymerizing two or more of the above monomers, i.e., graft copolymers of the vinyl monomer to the above polymers or copolymers are used. The vinyl monomer includes aromatic vinyl compounds such as styrene and α -methylstyrene, acrylic acid esters such as methyl acrylate and ethyl acrylate, methacrylic
- 45 acid esters such as methyl methacrylate and ethyl methacrylate, vinyl cyanide compounds such as acrylonitrile and methacrylonitrile, and vinyl esters such as vinyl acetate and vinyl propionate. One or more of these monomers are graft polymerized.
- Polymerization can be carried out by various methods such as bulk polymerization, suspension polymerization and emulsion polymerization. Polymers obtained by emulsion polymerization are particularly
- 50 preferred.
- Suitable examples of the rubber-like polymers in Group (I) are shown below.
- (1) Polymers obtained by polymerizing one or more of vinyl monomers in the presence of polymers containing alkyl acrylate and/or alkyl methacrylate (hereinafter referred to as "alkyl-acrylates") as main component.
- 55 Polymers containing alkyl acrylates as the main component are polymers obtained by polymerizing 70% or more by weight of alkyl acrylates and 30% or less by weight of other vinyl monomers copolymerizable with the alkyl acrylates, such as methyl methacrylate, acrylonitrile, vinyl acetate and styrene. Polymers obtained by using a suitable amount of a polyfunctional monomers, e.g., divinylbenzene,

ethylene dimethacrylate, triallyl cyanurate and triallyl isocyanurate as a cross-linking agent are also included in the above polymers.

A specific example of rubber-like polymers belonging to (1) is an MAS elastomer, obtained by graft polymerizing styrene to a copolymer of methyl methacrylate and butyl acrylate in a latex form. Such MAS elastomers are commercially available as EXL-2330 (trade name, produced by Rohm & Haas Co., Ltd., USA), KM-330 (trade name, produced by Rohm & Haas Co., Ltd., USA) and M-101 (trade name, produced by Kanegafuchi Kagaku Kogyo Co., Ltd.).

(2) Graft polymers obtained by copolymerizing one or more vinyl monomers to copolymers of alkyl acrylate and/or alkyl methacrylate and polyfunctional polymerizable monomers containing conjugated diene-type double bonds. In preparation of the graft polymers, as in the case of (1), vinyl monomers and a cross-linking agent can be added.

Specific examples of the rubber-like polymers belonging to (2) are; MABS elastomers, e.g. a graft copolymer obtained by adding styrene and methyl methacrylate to a rubber latex which has been obtained by copolymerizing octyl acrylate and butadiene (7:3) and then graft polymerizing them, and MBS elastomers, e.g. a graft copolymer obtained by adding styrene to a rubber latex which has been obtained by copolymerizing methyl methacrylate and butadiene and graft polymerizing them. As the MBS elastomer, Metablen C-223 (trade name, produced by Mitsubishi Rayon Co., Ltd.) is commercially available.

(3) Other elastomers include; an AABS elastomer, obtained by adding acrylonitrile and styrene to a rubber latex which has been obtained by copolymerizing butadiene and alkyl acrylate, and then graft polymerizing them, and a SBR elastomer (trade name Metablen IP-2, produced by Mitsubishi Rayon Co., Ltd.), obtained by graft polymerizing styrene to polybutadiene.

Group (II)

Polymers in Group (II) are rubber-like elastomers comprising one or more copolymers selected from a-b type block copolymers, a-b-a type block copolymers, b-a-b type block copolymers, a grafted b copolymers and b grafted a copolymers.

As portion a of the a-b, a-b-a or b-a-b type block copolymer, atactic polystyrene is preferred. Compatibility of the a-b, a-b-a or b-a-b type block copolymer with the component (A) is markedly high within the preferred range. As portion b, one or more polymers selected from conjugated diene, hydrogenated product of conjugated diene, conjugated diene modified with acid anhydride and hydrogenated product of conjugated diene modified with acid anhydride can be given. Examples of portion b include butadiene, isoprene, hydrogenated butadiene, hydrogenated isoprene, butadiene modified with maleic anhydride, hydrogenated product of butadiene modified with maleic anhydride, isoprene modified with maleic anhydride and hydrogenated product of isoprene modified with maleic anhydride can be given.

Graft copolymers which can be used are indicated in terms of a grafted b copolymers or b grafted a copolymers.

Portion a generally exhibits good affinity (dispersibility) to Component (A) in the block or graft copolymers comprising portions a and b. Examples of such rubber-like polymers are a styrene-butadiene block copolymer rubber (SB, SBS), rubbers obtained by partially or completely hydrogenating the butadiene portion of a styrene-butadiene block copolymer (SEBS), a styrene-isoprene block copolymer rubber (SI, SIS), rubbers obtained by partially or completely hydrogenating the isoprene portion of a styrene-isoprene block copolymer (SEP, SEPS), SBS modified with maleic, anhydride and SEBS modified with maleic anhydride.

Since these copolymers all have the styrene unit, they have good dispersibility in the styrene-based polymers with mainly syndiotactic configuration as Component (A). Thus, physical properties are markedly improved.

Group (III)

Rubber-like polymers such as natural rubber, polybutadiene, polyisoprene, polyisobutylene, neoprene, ethylene-propylene copolymer rubber, ethylene-propylene-diene methylene linkage copolymer rubber (EPDM), polysulfide rubber, thiokol rubber, acryl rubber, urethane rubber, silicone rubber, epichlorohydrin rubber, polyetherester rubber, and polyesterester rubber. These rubbers are not compatible with the styrene-based polymers having mainly syndiotactic configuration as Component (A). They are preferably used depending on the purpose of use of the resin composition of the present invention.

Rubber-like polymers to be used as Component (8) can be divided into the above groups (I) to (III). However, it is to be noted that the groups are not strictly divided and partially overlap with each other. One or more rubber-like polymers are used. More specifically, depending on the purpose of use of the resin composition and characteristics required, two or more rubber-like polymers selected from the same group can be used in combination, or two or more rubber-like polymers selected from different groups can be used in combination.

For example, when a rubber-like polymer belonging to Group (II) and a rubber-like polymer belonging to Group (III) are used in combination, they are chosen by considering that portion a of the rubber-like polymer of Group (II) exhibits good compatibility with Component (A) and portion b exhibits good compatibility with the rubber-like polymer of Group (III). If the rubber-like polymers of Groups (II) and (III) are used in combination, the compatibility between Components (A) and (B) is increased and the physical properties of the composition are effectively improved. The amount of the rubber-like polymer of Group (II) can be determined appropriately; it is preferably 0.05 to 50 parts by weight, more preferably 0.5 to 20 parts by weight per 100 parts of the total weight of Component (A) and the rubber-like polymer of Group (III). The amount of the rubber-like polymer of Group (II) is 5 to 95%, preferably 10 to 90% based on the total weight of the rubber-like polymers of Groups (II) and (III).

The particle size of the rubber-like polymer varies with the purpose of use of the composition or characteristics required therefor and cannot be determined unconditionally. In general, the average particle diameter (volume average particle diameter) of the rubber-like polymer in the composition is 0.1 to 4 μm and preferably 0.2 to 3 μm . Herein, volume average particle diameter (d) is defined by the following equation.

$$d = \Sigma d_i^4 / \Sigma d_i^3,$$

wherein d_i stands for a diameter of the i -th particle.

The proportion of Component (A) or (B) in the composition of the present invention is not critical and can be determined appropriately depending on the type of Component (B), the purpose of use of the composition, characteristics required therefor, and so forth. The composition usually comprises 65 to 99% by weight of Component (A) and 35 to 1% by weight of Component (B), and preferably 70 to 95% by weight of Component (A) and 30 to 5% by weight of Component (B).

In another embodiment of the present invention, the composition contains (C) an inorganic filler as well as Components (A) and (B). The inorganic filler may be fibrous, granular or powder in the form. Examples of the fibrous filler are glass fiber, carbon fiber, and alumina fiber. Of these fiber, glass fiber and carbon fiber are particularly preferred. The shape of the glass fiber is cloth-like, mat-like, strand-like, short fiber-like, and filament-like. Of these fibers, strand-like glass fiber having a length of 0.05 to 13 mm and a fiber diameter of 5 to 15 μm is preferred. Most preferable is the strand-like glass fiber subjected to silane treatment.

As the carbon fiber, polyacrylonitrile (PAN)-based fiber is preferred. Bundles of the chopped PAN fiber with a length of about 3 mm and a diameter of 7 to 15 μm are more preferable.

Examples of granular or powder inorganic fillers are talc, carbon black, graphite, titanium dioxide, silica, mica, calcium carbonate, calcium sulfate, barium carbonate, magnesium carbonate, magnesium sulfate, barium sulfate, oxysulfate, tin oxide, alumina, kaolin, silicon carbide, and metal powder. Of these fillers, titanium dioxide is most preferable. The crystal form of titanium dioxide is rutile, brucite or anatase. Titanium dioxide of the rutile or anatase structure, having an average particle diameter of 0.15 to 0.40 μm is preferred. It may be treated with Zn, Al, Si and the like.

In cases where Component (C) is added, the proportion of Component (A) or (B) can be chosen from a wide range. More specifically, the proportion of the component (A) in the composition is 1 to 98% by weight, preferably 5 to 95% by weight and most preferably 10 to 90% by weight. the proportion of Component (B) is 1 to 98% by weight, preferably 5 to 95% by weight and most preferable 20 to 80% by weight. The proportion of Component (C) is 1 to 60% by weight, preferably 5 to 50% by weight and most preferably 10 to 40% by weight.

The composition of the present invention is essentially composed of Components (A) and (B), or Components (A), (B) and (C). If necessary, various additives such as a nucleating agent, an antioxidant, a plasticizer, an ultraviolet ray inhibitor, a lubricant, a coloring agent, an antistatic agent, a thermal stabilizer, a flame retardant and the like can be added.

The composition of the present invention can be prepared by compounding Components (A) and (B), and other components if necessary, and kneading the resulting mixture at a suitable temperature, e.g., 270 to 320 $^{\circ}\text{C}$. Compounding and kneading can be carried out by usual methods. More specifically, the melt kneading method using a kneader, a mixing roll, an extruder, a Vanbury mixer, a Henschel mixer and

kneading roll, or the solution blending method can be employed.

The styrene-based resin composition of the present invention is excellent in heat resistance and at same time, in physical properties such as impact resistance, stiffness, tensile strength, and modulus in tension.

- 5 The styrene-based resin composition of the present invention is expected to be widely used as an industrial material for which heat resistance and various physical properties are required, particularly as raw material for injection molding or extrusion molding.

The present invention is described in greater detail with reference to the following examples.

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REFERENCE EXAMPLE 1

(Preparation of Polystyrene having Syndiotactic Configuration)

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2 L (L = liter) of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and 15 L of styrene was introduced thereto and polymerized for 4 hours at 50 °C.

- 20 After the completion of polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 2.5 kg of a styrene polymer (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The weight average molecular weight of the polymer was 800,000. A ¹³C-NMR analysis (solvent: 1,2-dichlorobenzene) showed an absorption at 145.35 ppm, ascribable to the syndiotactic configuration, and the syndiotacticity indicated in terms of racemic pentad as calculated from the peak area was 96%.
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EXAMPLE 1

- 30 90 parts by weight of the polystyrene having syndiotactic configuration obtained in Reference Example 1, 10 parts by weight of a styrene-hydrogenated butadiene block copolymer (trade name: G-1652, produced by Shell Chemical Co., Ltd.) as a rubber-like polymer, 0.1 part by weight of bis(2,4-di-tert-butylphenyl)-pentaerythritol diphosphite, 0.7 part by weight of tetraakis (methylene(3,5-di-tert-butyl-4-hydroxy-hydrocin-
namate))methane, and 0.5 part by weight of talc having an average particle diameter of 0.5 μm were
35 kneaded and pelletized by the use of a twin-screw extruder. These pellets were injection molded to form a test piece, which was then measured for Izod impact strength (notched) and modulus in tension. The results are shown in Table 1.

EXAMPLES 2 AND 3

- 40 The procedure of Example 1 was repeated with the exception that the proportions of the polystyrene having syndiotactic configuration as obtained in Reference Example 1 and the styrene-hydrogenated butadiene block copolymer (trade name G-1652, produced by Shell Chemical Co., Ltd.) as the rubber-like
45 polymer were changed as shown in Table 1. The results are shown in Table 1.

COMPARATIVE EXAMPLE 1

- 50 The procedure of Example 1 was repeated with the exception that the styrene-hydrogenated butadiene block copolymer was not used. The results are shown in Table 1.

EXAMPLE 4

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The procedure of Example 2 was repeated with the exception that a methyl methacrylate-butyl acrylate-styrene copolymer (trade name: KM330, produced by Rhom & Haas Co., Ltd., USA) was used as the rubber-like polymer. The results are shown in Table 1.

EXAMPLE 5

The procedure of Example 2 was repeated with the exception that a styrene-butadiene block copolymer (trade name TR-1102, produced by Shell Chemical Co., Ltd.) was used as the rubber-like polymer. The results are shown in Table 1.

EXAMPLE 6

The procedure of Example 2 was repeated with the exception that polybutadiene (trade name: NF35AS, produced by Asahi Kasei Co., Ltd.) was used as the rubber-like polymer. The results are shown in Table 1.

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Table 1

No.	Composition				Physical Properties	
	Styrene Polymer (wt%)	Type	Amount (wt%)	Volume Average Particle Diameter (μm)	Izod Impact Strength (notched) ($\text{kg}\cdot\text{cm}/\text{cm}$)	Modulus in Tension (kg/cm^2)
Example 1	90	SEBS ^{*1}	10	2.0	4.2	38000
Example 2	80	SEBS	20	2.5	7.3	34000
Example 3	70	SEBS	30	3.0	12.1	30000
Example 4	80	MA ^{*2}	20	0.3	8.0	35000
Example 5	80	SBS ^{*3}	20	2.5	5.4	32000
Example 6	80	Polybutadiene	20	3.5	3.8	30000
Comparative Example 1	100	-	-	-	2.2	40000

*1 Styrene-hydrogenated butadiene block copolymer

*2 Methyl methacrylate-butyl acrylate-styrene copolymer

*3 Styrene-butadiene block copolymer

EXAMPLE 7

100 parts by weight of a mixture consisting of 66.7% by weight of the polystyrene having syndiotactic configuration as obtained in Reference Example 1, 28.6% by weight of an ethylene-propylene rubber (trade name: EPO2P, produced by Nippon Synthetic Rubber Co., Ltd.) and 4.7% by weight of a styrene-hydrogenated butadiene block copolymer (trade name: G-1652, produced by Shell Chemical Co., Ltd.) and 1 part by weight of talc (trade name: FFR; average particle diameter; 0.6 μm , produced by Asada Seifun Co., Ltd.) were kneaded in a single-screw extruder having an inner diameter of 25 mm and injection molded by the use of a minimat molding machine to form a test piece, which was then measured for mechanical strength. The test piece was also measured for Vicat softening temperature according to JIS K 7206. The results are shown as follows.

Modulus in Tension :	30,000 kg/cm ²
Tensile Strength :	550 kg/cm ²
Izod Impact Strength (notched) :	11.7 kg \cdot cm/cm
Vicat Softening Temperature :	210 $^{\circ}$ C
Volume Average Particle Diameter of Rubber-Like Polymer in Composition:	3.5 μm

REFERENCE EXAMPLE 2

(Production of Polystyrene having Mainly Syndiotactic Configuration)

2 L of toluene as a solvent, and 5 mmol of tetraethoxy-titanium and 500 mmol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and 15 L of styrene was introduced thereinto and polymerized for 4 hours at 55 $^{\circ}$ C.

After the completion of polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 2.5 kg of a styrene polymer (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 97% by weight of an extraction residue. The weight average molecular weight of the extraction residue was 400,000. A ¹³C-NMR analysis (solvent: 1,2-dichlorobenzene) of the polymer showed an absorption at 145.35 ppm, ascribable to the syndiotactic configuration, and the syndiotacticity indicated in terms of racemi pentad as calculated from the peak area was 98%.

REFERENCE EXAMPLE 3

Commercially available granular resin elastomers (rubber-like polymers) were dispersed in acetone or methanol, sprayed to a micro mesh for observation under an electron microscope, and then observed under the electron microscope to determine the volume average particle diameter. The results are shown below.

(1) MAS Elastomer (trade name: KM-330, produced by Rohm & Haas Co., Ltd., USA)	0.3 μm
(2) MAS Elastomer (trade name: EXL-2330, produced by Rohm & Haas Co., Ltd., USA)	0.5 μm
(3) MAS Elastomer (trade name: M-101, produced by Kanegafuchi Kagaku Kogyo Co., Ltd.)	0.5 μm
(4) MBS Elastomer (trade name: C-223, produced by Mitsubishi Rayon Co., Ltd.)	0.4 μm
(5) MABS Elastomer (trade name: HIA-15, produced by Mitsubishi Rayon Co., Ltd.)	0.1 μm
(6) MAS Elastomer (trade name: W-529, produced by Kureha Kagaku Co., Ltd.)	0.2 μm

EXAMPLE 8

100 parts by weight of a mixture of 90% by weight of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2 and 10% by weight of a granular MAS elastomer (trade name EXL-2330, produced by Rohm & Haas Co., Ltd., USA), 1 part by weight of PTBBA-Al (aluminum p-tert-butyl-benzoate) as a nucleating agent, 0.7 part by weight of (2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite (trade name PEP-36, produced by Adeka Agas Corp.) as an antioxidant and 0.1 part by weight of 2,6-di-tert-butyl-4-methylphenol (trade name: Sumiriser BHT, produced by Sumitomo Kagaku Co., Ltd.) were kneaded and pelletized by the use of a twin screw kneading extruder.

The pellets thus obtained were injection molded to form a test piece, which was then measured for Izod impact strength (notched) (according to JIS K7110), modulus in tension (according to JIS K7113) and Vicat softening temperature (according to JIS K7206). The results are shown in Table 2.

A slice for examination under an electron microscope was cut away from the Izod test piece and observed by the phase contrast method. The particle diameter of the elastomer (rubber) as determined by the above method was 0.5 μm .

EXAMPLE 9

The procedure of Example 8 was repeated with the exception that a mixture of 80% by weight of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2 and 20% by weight of MAS elastomer (trade name: M-101, produced by Kanegafuchi Kagaku Co., Ltd.) was used. The results are shown in Table 2.

The rubber particle diameter as determined from a slice in the same manner as in Example 8 was 0.5 μm .

EXAMPLE 10

The procedure of Example 8 was repeated with the exception that a mixture of 70% by weight of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2 and 30% by weight of MBS elastomer (trade name: C-223, produced by Mitsubishi Rayon Co., Ltd.) was used. The results are shown in Table 2.

The rubber particle diameter as determined after dyeing a slice with osmic acid was 0.4 μm .

EXAMPLE 11

The procedure of Example 8 was repeated with the exception that a mixture of 80% by weight of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2, and 5% by weight of MBS elastomer (trade name C-223, produced by Mitsubishi Rayon Co., Ltd.) and 15% by weight of MABS (trade name: HIA-15, produced by Mitsubishi Rayon Co., Ltd.) as granular elastomers was used. The results are shown in Table 2.

The Izod test piece thus obtained was dissolved in hot xylene, and the gel portion was filtered and dried, dispersed in acetone and then observed under an electron microscope. Particles having a diameter of 0.4 μm and particles having a diameter of 0.1 μm were observed, and the area fraction in the observation area was about 1:3.

EXAMPLE 12

The procedure of Example 8 was repeated with the exception that a mixture of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2, and 2% by weight of MAS elastomer (trade name M-101, produced by Kanegafuchi Kagaku Kogyo Co., Ltd.) and 30% by weight of MAS elastomer (trade name: W-529, produced by Kureha Kagaku Co., Ltd.) was used. The results are shown in Table 2.

An electron microscopic examination after gel extraction showed particles having a diameter of 0.5 μm and particles having a diameter of 0.2 μm . The area fraction in the observation area was about 1:15.

EXAMPLE 13

The procedure of Example 8 was repeated with the exception that a mixture of 85% by weight of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2, and 10% by weight of MBS elastomer (trade name: C-223, produced by Mitsubishi Rayon Co., Ltd.) and 5% by weight of SBS elastomer (trade name: TR-1102, produced by Shell Chemical Co., Ltd.) as granular elastomers was used. The results are shown in Table 2.

An electron microscopic examination of the gel showed particles having a diameter of 0.4 μm .

EXAMPLE 14

50 parts by weight of polybutadiene having an average particle diameter of 1.0 μm , 20 parts by weight of styrene, 0.1 part by weight of potassium rhosinate, 0.1 part by weight of potassium hydroxide, 0.2 part by weight of sodium pyrophosphate, 0.3 part by weight of dextrose, 0.01 part by weight of ferrous sulfate and 150 parts by weight of water were placed in a reactor equipped with a stirrer. After purging with nitrogen, the temperature was raised to 70 °C, and 0.2 part by weight of cumene hydroperoxide was added to perform the polymerization for one hour.

An emulsion consisting of 30 parts by weight of styrene, 1.5 parts by weight of potassium rhosinate, 0.1 part by weight of potassium hydroxide, 0.2 part by weight of cumene hydroperoxide and 50 parts by weight of water was separately prepared and added to the polymerization system over 3 hours.

The polymerization reaction was continued for one hour while maintaining the jacket temperature at 70 °C.

To the latex above obtained were added 1.0 part by weight of 2,6-di-tert-butyl-p-cresol as an anti-aging agent and 2.0 parts by weight of sulfuric acid. The latex was solidified by heating, filtered, washed with water and dried to obtain a granular elastomer (SBR). The particle diameter was 1.2 μm .

Thereafter, the procedure of Example 8 was repeated with the exception that a mixture of 10% by weight of the above granular elastomer and 90% by weight of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2 was used. The results are shown in Table 2.

EXAMPLE 15

70 parts by weight of a polybutadiene latex having an average particle diameter of 2.4 μm , 200 parts by weight of water and 0.3 part by weight of potassium persulfate were placed in a reactor, and 15 parts by weight of methyl methacrylate was dropped over 30 minutes while maintaining the temperature at 70 °C to perform polymerization. After the completion of dropwise addition, the polymerization was completed by maintaining at the same temperature for one hour.

Then, 15 parts by weight of styrene was dropped over 30 minutes to perform polymerization, and the polymerization was completed by maintaining for 60 minutes.

The average particle diameter of the graft copolymer latex as obtained above which was determined by an electron microscopic observation was 2.5 μm .

Subsequently, the graft copolymer latex was salted and solidified by adding an aqueous aluminum chloride solution, filtered, washed with water and dried to obtain a granular elastomer.

Thereafter the procedure of Example 8 was repeated with the exception that a mixture of 10% by weight of the above granular elastomer and 90% by weight of the styrene polymer having syndiotactic configuration as obtained in Reference Example 2 was used. The results are shown in Table 2.

Table 2

No.	Composition						
	Styrene Polymer (wt%)	Granular Elastomer having Volume Average Particle Diameter of 0.35 μm or more			Other Rubber-Like Polymer		
		Type	Particle Diameter (μm)	(wt%)	Type	Particle Diameter (μm)	(wt%)
Example 8	90	MAS	0.5	10	-	-	253
Example 9	80	MAS	0.5	20	-	-	244
Example 10	70	MBS	0.4	30	-	-	232
Example 11	80	MBS	0.4	5	MABS	0.1	237
Example 12	68	MAS	0.5	2	MAS	0.2	228
Example 13	85	MBS	0.4	10	SBS	shapeless	240
Example 14	90	SBR	1.2	10	-	-	250
Example 15	90	MBS	2.5	10	-	-	248

1) EXL-2330,
2) M-101,
3) C-223,
4) HIA-15
5) W-529,
6) TR-1102

REFERENCE EXAMPLE 4

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(Production of Polystyrene having mainly Syndiotactic Configuration)

2 L of toluene as a solvent, and 1 mmol of cyclopentadienyltitanium trichloride and 0.8 mol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and 3.6 L of
 10 styrene was added and polymerized at 20 °C for one hour. After the completion of polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 330 g of a polymer.

This polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95%
 15 by weight of an extraction residue. The polymer (extraction residue) had a weight average molecular weight of 290,000, a number average molecular weight of 158,000 and a melting point of 270 °C. A ¹³C-NMR analysis of the polymer showed an absorption at 145.35 ppm, ascribable to the syndiotactic structure, and the syndiotacticity indicated in terms of pentad as calculated from the peak area was 96%.

20 EXAMPLE 15

35 parts by weight of the polystyrene having syndiotactic configuration as obtained in Reference Example 4, 35 parts by weight of a methyl methacrylate-n-butyl acrylate-styrene copolymer (trade name: KM330, produced by Rohm & Haas Co., Ltd., USA) and 30 parts by weight of glass fiber having an average
 25 fiber length of 3 mm (produced by Asahi Fiberglass Co., Ltd.; fiber diameter: 10 to 15 μm; chopped strand form) were dry blended, and then 1 part by weight of talc (trade name: Talc FFR, produced by Asada Seifun Co., Ltd.) as a crystal nucleating agent was added. They were mixed in a Henschel mixer, and then kneaded, extruded and pelletized by the use of an extruder. The pellets thus obtained were molded to form a test piece, which was then measured for mechanical strength and heat distortion temperature. The
 30 modulus in tension was 83,000 kg/cm², the tensile strength was 870 kg/cm², and the heat distortion temperature was 220 °C.

Claims

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1. A styrene-based resin composition containing (A) a styrene-based resin with mainly syndiotactic configuration and (B) a rubber-like polymer as main components.

2. The composition as claimed in Claim 1, comprising 65 to 99% by weight of the styrene-based resin (A) and 35 to 1% by weight of the rubber-like polymer (B).

40 3. The composition as claimed in Claim 1 wherein the rubber-like polymer (B) is a polymer produced by polymerizing vinyl monomers in the presence of polymers obtained through polymerization of one or more monomers selected from the group consisting of alkyl acrylate, alkyl methacrylate and polyfunctional monomers having conjugated diene-type double bonds.

45 4. The composition as claimed in Claim 1 wherein the rubber-like polymer (B) is at least one block or graft copolymer selected from an a-b type block copolymer, an a-b-a type block copolymer, a b-a-b type block copolymer, an a grafted b copolymer and a b grafted a copolymer; wherein a is atactic polystyrene, and b is at least one polymer selected from conjugated diene, hydrogenated product of conjugated diene, conjugated diene modified with acid anhydride and hydrogenated product of conjugated diene modified with acid anhydride.

50 5. The composition as claimed in any of Claims 1 to 4 wherein the volume average particle diameter of the rubber-like polymer (B) is 0.1 to 4 μm.

6. A styrene-based resin composition containing (A) a styrene-based resin having mainly syndiotactic configuration, (B) a rubber-like polymer and (C) an inorganic filler.

55 7. The composition as claimed in Claim 6, comprising 1 to 98% by weight of the styrene-based polymer (A), 1 to 98% by weight of the rubber-like polymer (B), and 1 to 60% by weight of the inorganic filler (C).

8. The composition as claimed in Claim 6 wherein the volume average particle diameter of the rubber-like polymer (B) is 0.1 to 4 μm .

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 88 11 9375

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	CHEMICAL ABSTRACTS, vol. 108, no. 18, 2nd May 1988, page 49, abstract no. 151651n, Columbus, Ohio, US; & JP-A-62 257 950 (IDEMITSU KOSAN CO., LTD) 10-11-1987 (Cat. X) * Abstract *	1,2	C 08 L 25/02 // (C 08 L 25/02 C 08 L 51:00) (C 08 L 25/02 C 08 L 53:00)
X	DE-A-1 297 328 (HÜLS AG) * Claims *	1-8	
X	FR-A-2 311 645 (HÜLS AG) * Claims *	1-8	
X	FR-A-2 259 874 (SUMITOMO) * Claims *	1-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-03-1989	Examiner HOFFMANN K.W.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			